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SYNTHESIS AND CHARACTERIZATION OF NANO $La_{0.6}Pb_{0.4-x}Ca_xMnO3$ ($0.005 \leq x \leq 0.015$) PEROVSKITEMAGNATITE MATERIALS

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ABSTRACT

Due to the versatile applications of perovskite manganite materials in fuel cells and sensors, research on two divalent doped perovskite magnetite materials are encouraging due to its interesting structural, magnetic and electrical properties. An effort has made to synthesis and characterization of nano $La_{0.6}Pb_{0.4-x}Ca_xMnO3$ ($0.005 \leq x \leq 0.015$) perovskite magnetic materials. The above perovskite have been prepared in bulk and nanoscale by using solid state and sonochemical reaction methods respectively. The prepared samples were characterised by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscope, Energy Dispersive X-Ray Microanalysis and Transmission electron microscopy structural investigations presented. The observed XRD results indicate that the prepared bulk and nano samples are in the rhombohedral crystal structure. The measurement of density of prepared bulk and nano samples were also carried out. The estimated particle size of bulk and nano perovskites is 352 nm and 90 nm respectively.

KEYWORDS: Perovskites, Solid State Reaction, Sonochemical Reactor, Rhombohedral

INTRODUCTION

Perovskite magnetic nanomaterials were used as a magnetic storage device in sensor technology, frequency switching devices in electronic industries and as a electrode in fuel cells and batteries. Due to its potential applications, the perovskite manganite materials were studied with various compositions (1, 2).The research on $Ln_{1-x}A_xMnO3$ perovskites (Ln=rare earth, A= divalent element) have strongly attracted by many researchers (3). Young et al. [4] have studied the crystal structure and magnetic properties of $La_{0.7}Pb_{0.3}Mn_{1-x}Co_xO_3$ perovskites for the composition of x ($0 \leq x \leq 1$). For x = 0theseauthorsfounda rhombohedral structure and also a rather large magneto resistance effect, about 50% below 200 K and about 25% around 300. Troyanchuk et al. [5] have observed that the $La_{1-x}Pb_xMnO3$ perovskites (x = 0.4-0.6) have a rhombohedral (slightly distorted) cubic structure. Huang et al.[6] have studied the crystal structure and the magnetic scaling behaviourof$La_{1-x}Pb_xMnO3$ perovskites(x=0.0-0.5) and have shown that all the samples crystallize in the rhombohedral structure. Nguyen Chau et al.have investigated the structural and magnetic properties of prepared $La_{1-x}Pb_xMnO3$(x = 0.1, 0.2, 0.3, 0.4, and 0.5) perovskites samples. Forx = 0.4rhombohedral structure was observed,where as fortheothercompositionsit was pseudo-rhombohedralwithP_1symmetry. In all cases,it is clear that, the particle size of the grains depends on the Pb content of the samples[7]. It was a well known fact that the structural, magnetic and electronic properties were sensitive to external parameters, such as magnetic field, temperature and pressure. In this study doped divalent element variations in pervoskite manganite materials were carried out to study its effect on structural properties. In the present study, the synthesis and structural studies on $La_{1-x}Pb_xMnO3$ manganite with $La_{0.6}Pb_{0.4-x}Ca_xMnO3$ ($0.005 \leq x \leq 0.015$) were carried out. Materials were prepared in two methods such as solid state reaction method was adopted for preparation of bulk materials and while the sonochemical reactor method was employed for nano materials.

EXPERIMENTAL PROCEDURE

High purity powders of La_2 (NO_3) $_3.6H_2O$ (MERCK 99%), Pb (NO_3) $_2$ (MERCK 99%), $CaCO_3$ (SRL 99.5%) and $MnCO_3$ (Aldrich 99.9%) were weighed using a digital balance in appropriate proportions to obtain the compositions of $La_{0.6}$ $(Pb_{0.\ 4-x}Ca_x)$ MnO3 (LPCMO) was prepared by using the solid state reaction technique with values of x=0. 005, 0.01, 0.015. The bulk and nano material were prepared elsewhere discussed [8]. The crystal structures of the bulk and nano perovskite samples were examined by recording the X-ray diffraction (XRD) pattern by using the powder X-ray diffractometer (X' Pert Pro, Analytical, Netherlands). The patterns were obtained using CuKα as a radiation source by applying voltage and current ratings of 40 kV and 30 mA. Fourier transformation infrared (FTIR) absorption spectra of the bulk perovskite were recorded on the room temperature from 4000 to 400 cm^{-1} using a FTIR spectrometer (Spectrum 100, PerkinElmer, USA). The sample and high spectrum grade KBr were mixed with 1:100 weight ratios in an agate mortar and then, pressed into a pellet of 13 mm diameter and 0.5 mm thickness. The scanning electron microscope (SEM) coupled with the energy-dispersive analysis X-rays (EDAX) (JEOL, JSM 5300) was used to obtain a surface image of the bulk and nano samples to explore morphology, microstructure and composition of perovskites samples. Similarly, transmission electron microscope (TEM, Philips, CM 200, USA) was used to obtain the sub structural information and particle size of the bulk and nano samples. Archimedes' method principle was employed to measure the density of the prepared perovskite samples. The density of bulk and nano perovskites was calculated by measuring the weight sample in air and CCl_4 (buoyant) [9].

RESULTS AND DISCUSSIONS

The recorded XRD patterns of bulk and nano samples are shown in Figure 1. It is inferred that the observed XRD patterns of the bulk sample reveals a crystalline nature namely rhombohedral phases as reported elsewhere [10, 11]. All the peaks observed for bulk and nano LPCMO correspond to rhombohedral phase. Nevertheless, the diffraction peaks observed in the bulk LPCMO samples are quite broad in nature, indicating a crystalline nature. On the other hand, in nano sample, the peaks are very narrow and slightly shifted towards its lower 2θ values which indicate the nano crystalline nature of the sample. The decrease in diffraction peak width (FWHM) for (1 1 0) planes in the nano sample confirms the decrease in nano crystalline size upon sintering. The observed results indicate a decrease in the crystalline size, while comparing the nano sample with the bulk sample.

FTIR studies are done in the bulk LPCMO samples. The FTIR spectrum of the bulk and nano LPCMO samples is given in Figure 2a & b. The observed band at 600 cm^{-1} corresponds to stretching mode which involves the internal motion of change in Mn–O–Mn bond length [12]. A

Br oad peak observed at 1630cm^{-1} reveals the deformation and O-H stretching mode of absorbed water molecules [13]. The energy dispersive analysis of X-ray (EDAX) confirms the composition of the constituent elements (figure 3) present in the samples. The molar ratio of elements La, Pb, Ca, Mn and O are, respectively, 0.005, 0.01and 0.015 in the bulk and nano samples. The EDAX based chemical composition values well matched with the atomic composition of the starting materials used for the preparation of perovskite materials. The SEM image of the bulk and nano samples is shown in Figure 4. SEM micrograph of bulk sample reveals that the obtained LPCMO samples are voluminous and porous in view of the large amount of gases evolved during the sonication and preheat treatments. It is evident from that the existence of irregular shapes of agglomerates along with the cage-structure in the bulk sample. Due to the elongated aggregates and poorly defined boundaries, the grain size determination of particles is difficult from the observed SEM images. It is evident from the observed XRD and FTIR results, the bulk sample contains a mixture of crystalline structures

of rhombohedral [14, 15] and O–H stretching mode of absorbed water molecules [16]. Generally, during the sintering, the crystalline size increases while the surface area of the particles decreases. However, in the nano sample, the particle size 90 nm due to agglomeration effects of the existence of rhombohedral phase instead of mixed structure as observed in the bulk sample. A decrease in the nano sample is reported elsewhere [17, 18]. Therefore, a decrease in the particle size is observed in the nano samples leads to a decrease in surface area when compared to bulk sample. The TEM images of the bulk and nano samples are shown in Figure 5. The TEM studies also confirm a decrease in particle size upon sintering as discussed earlier from the results of XRD and SEM results.

CONCLUSIONS

Nano $La_{0.6}Pb_{0.4-x}Ca_xMnO3$ ($0.005 \leq x \leq 0.015$) perovskite magnetic materials was synthesized along with the bulk samples with same composition. From the XRD results it is conformed that both samples has rhombohedral phase with crystalline nature. The FTIR study reveals the different possible modes in the prepared samples. Surface morphology was well conformed by SEM images. Decrease in the particle size is observed in the nano samples leads to a decrease in surface area when compared to bulk sample. The TEM studies also confirm a decrease in particle size upon sintering.

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APPENDICES

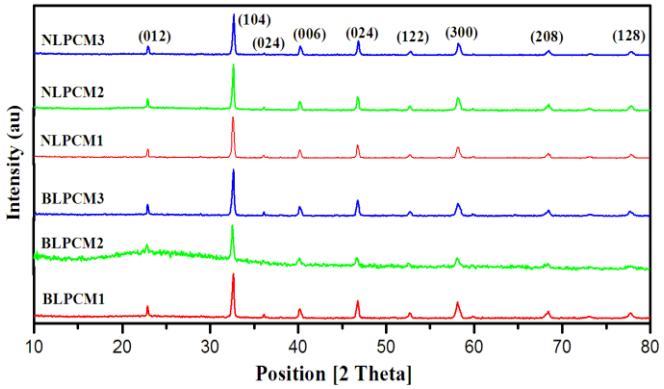

Figure 1: XRD Pattern of Bulk La0.6Pb0.395Ca0.005MnO3 (BLPCM1), Bulk La0.6Pb0.390Ca0.01MnO3 (BLPCM2), Bulk La0.6Pb0.385Ca0.015MnO3 (BLPCM3), Nano La0.6Pb0.395Ca0.005MnO3 (NLPCM1), Nano La0.6Pb0.390Ca0.01MnO3 (NLPCM2) La0.6Pb0.385Ca0.015MnO3 (NLPCM2) Perovskite Samples

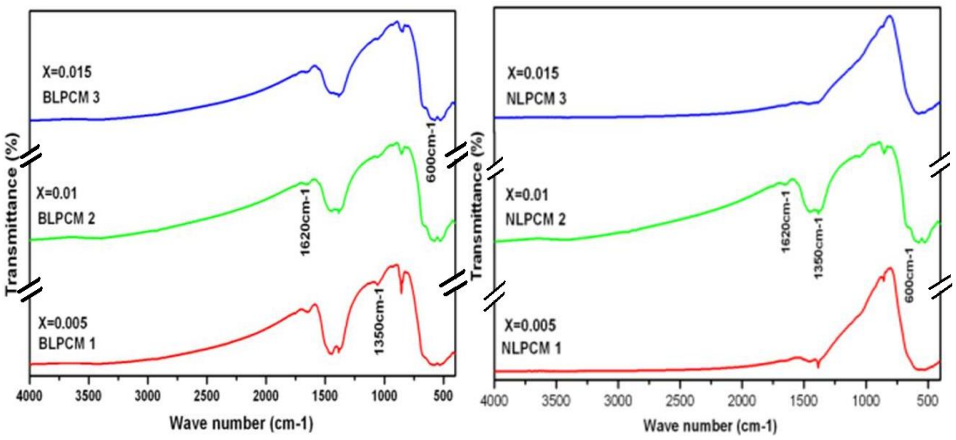

Figure 2a **Figure 2b**

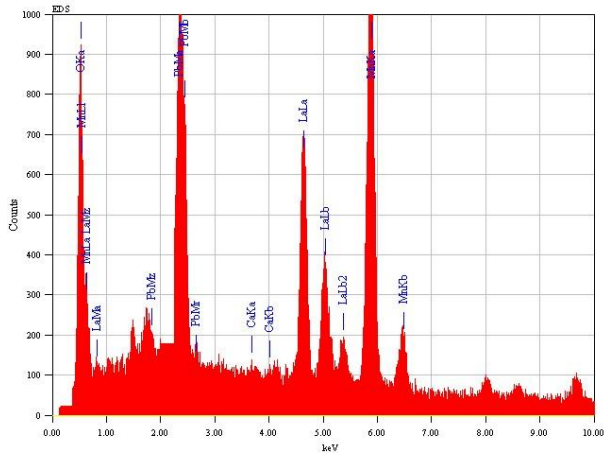

Figure 3

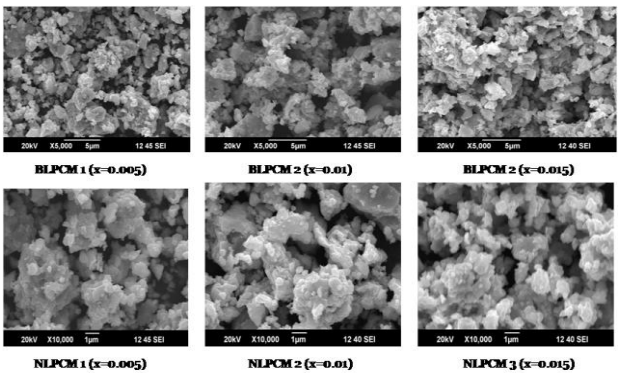

Figure 4

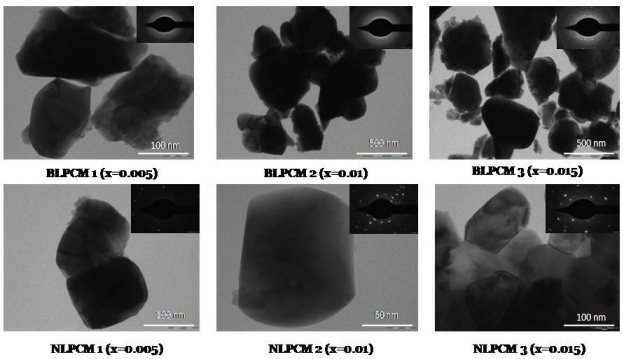

Figure 5